CRYSTALLIZATION CHARACTERISTIC OF PENTAERYTHRITOL TETRALAURATE

SHAHBUDIN BIN SOBKI

Faculty of Chemical Engineering & Natural Resources
University College of Engineering & Technology Malaysia

NOVEMBER 2006

CRYSTALLIZATION CHARACTERISTIC OF PENTAERYTHRITOL TETRALAURATE

SHAHBUDIN BIN SOBKI

A thesis submitted in fulfillment of the
Requirements for the award of the degree of
Chemical Engineering & Natural Resources

Faculty of Chemical Engineering & Natural Resources
University College of Engineering & Technology Malaysia

NOVEMBER 2006

DECLARATION

I declare that this thesis entitled “Crystallization Characteristic of Pentaerythritol Tetralaurate” is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : .....

Name : SHAHBUDIN BIN SOBKI

Date : 20 NOVEMBER 2006

ACKNOWLEDGEMENT

First of all, I would like to express my appreciation especially to my loving father, Mr Sobki bin Othman, my very supporter sister, Ms. Norlaili binti Sobki and rest of my family members who are very supportive morally to whatever good thing that I have involved and done all these years.

Secondly, I would like to thank to my final year project supervisor Mr. Sabri bin Mahmud for his understanding, guidance ideas unforgettable advice and moral support in making and finishing this project reality. I also would like to thank to the lectures at Faculty of Chemical and Natural Resources Engineering and all the Teaching Engineers have been teaching me all this while.

Lastly, not forgotten to my partners friends Mr Riduan bin Abd Ghani, Mr Shahrulnizam bin Jamen, Mr Mohd Fadli bin Abdullah and also to my others fellow undergraduate who are helpful especially ideas, valuable opinions and advice during the progress of this project. My sincere appreciations also extend to all my colleagues and others who have provided assistance at various occasions. Their views and tips are useful indeed. Thank you.

To my beloved mother and father.

ABSTRACT

Crystallization of pure Pentaerythritol Tetralaurate (PETD) can be done by using melt crystallization technique. PETD is important chemical used as an essential varnish additive in magnetic wire production and has high demand in Malaysia industry such as Kaneka Chemical. The technology to crystallize PETD has not been localized yet, and study the characteristic of PETD crystal will help industry to store this chemical. PETD is a new chemical produced for a few years ago and the physical property of PETD has not known, made the crystallization process more difficult to handle because of this lack of knowledge. In this study, the melt crystallization technique was used for pure substance crystallization. The crystallization process used temperature as the parameter to study their time of crystallization. The crystals that had been produced then were analyzed by Scanning Electron Microscope (SEM). The SEM micrograph can view the crystals size at magnifier 120 and 200. The result from SEM showed the topography and morphology of PETD crystal which direct water contact cooling method gave circle shape crystal and non-direct water contact cooling method had the crystal shape looked like it container.

ABSTRAK

Penghabluran Pentaerythritol Tetralaurate (PETD) boleh dilakukan dengan menggunakan teknik penghabluran lebur. PETD adalah bahan kimia penting digunakan sebagai varnis tambahan dalam menghasilkan wayar bermagnet dan mempunyai permintaan yang tinggi dalam industri Malaysia seperti Kaneka Chemical. Teknologi untuk penghabluran PETD masih tidak diketahui, membuatkan proses penghabluran lebih sukar untuk dilakukan disebabkan kekurangan pengetahuan bahan kimia ini. Proses penghabluran menggunakan suhu sebagai parameter untuk kajian masa penghabluran. Hablur yang telah dihasilkan kemudian dianalisa oleh alat Scanning Electron Microscope (SEM). Micrograph SEM boleh melihat hablur pada pembesaran 120 dan 200. Keputusan dari SEM menunjukkan topography dan morphology hablur PETD di mana kaedah penyejukan penyentuhan air secara langsung memberi bentuk hablur bulat dan penyejukan penyentuhan air secara tidak langsung menghasilkan hablur berbentuk seperti bekasnya.

TABLE OF CONTENTS

CHAPTER	TITLE		PAGE
	ABSTRACT		**i**
	ABSTRAK		**ii**
	TABLE OF CONTENTS		**iii**
	LIST OF FIGURES		**iv**
	LIST OF SYMBOLS		**v**
1.0	**INTRODUCTION**		
	1.1	Overview of research	1
	1.2	Problem Statement	2
	1.3	Research Objective & scope	3
	1.4	Research Contribution	3
	1.5	Thesis Layout	4
2.0	**LITERATURE REVIEW**		
	2.1	Introduction	5
	2.2	Types of crystal geometry	5
	2.3	Crystallization from melt	7
	2.4	Crystallization Theory	8
		2.4.1 Nucleation	8

2.4.1.1 Solubility and crystal size 9
2.4.1.2 Homogenous nucleation 9
2.4.1.3 Contact nucleation 9
2.4.1.4 Nucleation in commercial crystallizer 10
2.4.2 Crystal growth theories 10
2.5 Scanning Electron Microscope 11
2.5.1 Scanning process 11
2.5.2 Detection of secondary electrons 12
2.5.3 Detection of backscattered electrons 12
2.5.4 Beam injection analysis of semiconductors 13
2.5.5 Resolution of Scanning Electron Microscope (SEM) 14

3.0 RESEARCH METHODOLOGY

3.1 Introduction 15
3.2 Experiment: Direct contact cooling method 17
3.3 Direct water contact cooling 18
3.4 Analysis 21

4.0 RESULTS AND DISCUSSION

4.1 Direct water contact cooling 23
4.2 Non-direct water contact cooling 25
4.3 Analysis 26
4.4 Morphology study 31

5.0 RECOMMENDATION AND CONCLUSION

5.1 Recommendation 32

5.2 Conclusion 32

REFERENCE **34**

APPENDICE A **36**

LIST OF FIGURES

FIGURE NO	TITLE	PAGE
3.1	Research methodology	16
3.2	Crystallization at 20°C	20
3.3	Crystallization at 12°C	20
3.4	Crystallization at 0°C	21
4.1	Crystal by direct water contact cooling	24
4.2	Crystal by direct water contact cooling	24
4.3	Graph temperature effect on crystallization time	25
4.4	Crystal by non-direct water contact cooling	26
4.5	Crystal by non-direct water contact cooling	26
4.6	sample 1 (120 X)	27
4.7	sample 1 (250 X)	28
4.8	sample 2 (120 X)	28
4.9	sample 2 (250 X)	29
4.10	sample 3 (120 X)	29
4.11	sample 3 (250 X)	30
4.12	sample 4 (120 X)	30
4.13	sample 4 (250 X)	31

LIST OF SIMBOLS

PETD = Pentaerythritol Tetralaurate

SEM = Scanning Electron Microscope

FKKSA = Faculty of Chemical and Natural Resource Engineering

FKM = Faculty of Mechanical Engineering

nm = nanometer

µm = micrometer

mm = milimeter

min = minute

s = second

ml = milliliter

% = percent

g = gram

°C = degree celcius

in = inch

kV = kilovolt

LIST OF TABLES

TABLE NO	TITLE	PAGE
3.1	ZEISS EVO 50 Specification	22
4.1	Result data of non-direct water contact cooling	25

CHAPTER 1

INTRODUCTION

1.1 Overview of Research

Pentaerythritol Tetralaurate or Pentaerythritol Dodecanoate (PETD) has been used as varnish additive in production of magnetic wire for a few years ago and recently has been conducted at foreign country using esterification process. In Malaysia, this product is important to chemical company such as Kaneka Chemical. The chemical recently produced and supplied directly from Japan because local company still has not known the technology to produce the fine chemical at an optimum output in Malaysia yet.

Crystallization is a process where solid particles are formed from a homogeneous phase. This process can occur in the freezing of water to form ice, in the formation of snow particles from a vapor, in the formation of solid particles from a liquid melt, or in the formation of the solid crystals from a liquid solution. In crystallization the solution is concentrated and usually cooled until the solute concentration becomes greater than its solubility at that temperature. Then the solute comes out of the solution, forming crystals of approximately pure solute [1].

The term ‘melt’ strictly refers to a liquid close to its freezing point, but in general industrial application it tends to encompass multicomponent liquid mixtures that solidify on cooling. Melt crystallization is a common term applied to the controlled cooling

crystallization and separation of such systems with the objective of producing one or more of components in relatively pure form [2].

1.2 Problem Statement

Many of the difficulties facing designers of industrial crystallizers arise from the shortage of basic data in the technical literature. However, not only are published data limited, they are so frequently unreliable. It is not uncommon to find different investigators reporting crystal growth rates for the same substance differing by an order of magnitude or more. In such cases it is often impossible to select the appreciate value for a given situation, usually because some important parameter has not been specified, or perhaps not even measured. Reliable nucleation data applicable to industrial systems are seldom, if ever, available in the literature [2].

The unit operation of crystallization is governed by some very complex interacting variables. It is a simultaneous heat and mass transfer process with a strong dependence on fluid and particle mechanics. It takes place in a multiphase, multicomponent system. It is concerned with particulate solids whose size and size distribution, both incapable of unique definition, vary with time. The solids are suspended in a solution which can fluctuate between metastable equilibrium and a labile state, and the solution composition can also vary with time. The nucleation and growth kinetics, the governing processes in this operation, can often be profoundly influenced by mere traces of impurity in the system; a few parts per million may alter the crystalline product beyond all recognition [2].

It is perhaps no wonder that crystallization was once called an art rather than a science, but to do so today would be to ignore the tremendous advances that have been made over the past three or more decade in both the theory and practice of the subject [2]

1.3 Research Objective & Scope

The aim of this study is to determine the characteristic of PETD crystal. To achieve the objective of this research, there are two scopes that have been identified:

i. To study the time of crystallization by effect of temperature.
ii. To study PETD crystal characteristic by using electron microscopy to observe:
    a) topography
    b) morphology

1.4 Research Contribution

After finish doing this research, hopefully this research will be a pioneer of crystallization of PETD and give knowledge to other people. The successful of this crystallization technique will help industry in Malaysia to crystallize PETD. This chemical is usefull as an essential varnish additive in magnetic wire production.

1.5 Thesis Layout

Basically, chapter 1 will cover all about introduction. Here, some basic review about the crystallization and knowledge about crystal will be generalized. The second chapter will go further about the thesis, and it is so-called literature review, say about sub chapters. The third chapter will be going into methodology on how this research will be done. The fourth chapter will be going deep into this research, to discuss the result according to the literature review. All the data will analyze in this chapter. The last chapter is the conclusion, which answer the objective achievement from this research.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In commercial crystallization not only are the yield and purity of the crystals important but also the sizes and shapes of the crystals. It is often desirable that crystal be uniform in size. Size uniformity is desirable to minimize caking in the package, for ease of pouring, for ease in washing and filtering, and for uniform behavior when used. Sometimes large crystals are requested by the purchaser, even though smaller crystals are just as useful. Also, crystals of a certain shape are sometimes required, such as needles rather than cubes [1].

2.2 Types of crystal geometry

A crystal can be defined as a solid composed of atoms, ions, or molecules which are arranged in an orderly and repetitive manner. It is highly organized type of matter. The atoms, ions, or molecules are located in three-dimensional arrays or space lattices. The inter atomic distances between these imaginary planes or space lattices in a crystal

are measured by X-ray diffraction, as are the angles between these planes. The pattern or arrangement of these space lattices is repeated in all directions [1].

Crystals appear as polyhedron having flat faces and sharp corners. The relative sizes of the faces and edges of different crystals of the same material may differ greatly. However, the angles between the corresponding faces of all crystals of the same material are equal and are characteristic of that particular material. Therefore, crystals are classified on the basis of these interfacial angles [1].

There are seven classes of crystals, depending upon the arrangement of the axes to which the angles are referred [1]:

1. Cubic system. Three equal axes at right angles to each other.
2. Tetragonal system. Three axes at right angles to each other, one axis longer than the other two.
3. Orthorhombic system. Three axes at right angles to each other, all of different lengths.
4. Hexagonal system. Three equal axes in one plane at 60° to each other, and a fourth axis at right angles to this plane and not necessarily the same length.
5. Monoclinic system. Three unequal axes, two at right angles in a plane and a third at some angle to this plane.
6. Triclinic system. Three unequal axes at unequal angles to each other and not 30, 60, or 90°.
7. Trigonal system. Three equal and equally inclined axes.

The relative development of different types of faces of a crystal may differ depending on the solute crystallizing. The crystallization in overall shapes of plates or needles has no

relation to the type of crystal system and usually depends upon the process condition under which the crystals are grown.

2.3 Crystallization from melt

The term ‘melt’ strictly refers to a liquid close to its freezing point, but in general industrial application it tends to encompass multicomponent liquid mixtures that solidify on cooling. Melt crystallization is a common term applied to the controlled cooling crystallization and separation of such systems with the objective of producing one or more of components in relatively pure form [2].

There are some techniques that call zone melting. The techniques are very important in industrial crystallizations. For example large single crystals of silicium are grown by zone melting, which then can be used as semiconductors [4]. These techniques also useful to grow single crystals for x-ray structure determination. Especially compounds with low melting points are suitable here, that means mainly compounds which are liquid at room temperature [4].

To create the zone melting, the compound of interest is filled into a glass capillary of 0.2-0.3 mm diameter. The capillary should be sealed on both ends. With the help of the low temperature equipment of the diffractometer the substance is cooled down until it solidifies to a microcrystalline powder. The temperature is then raised again until approximately 15 K below the melting point of the compound. At this temperature the zone melting is performed [4].

The heat for the zone melting is generated by an ordinary lamp (for example from a slide projector). The light of the lamp is focused onto the capillary by the use of a concave mirror. This mirror is mounted movable, so that the focus can be moved up and

down the capillary. The movement can be done manually or driven by a computer. In a first step there must be a crystal seed in the capillary, which is generated from the microcrystalline powder. This crystal seed can afterwards be grown by zone melting to a suitable crystal for x-ray diffraction [4].

2.4 Crystallization Theory

If the solubility data for a substance in a particular solvent are known, it is a simple matter to calculate the maximum yield of pure crystals that could be obtained by cooling or evaporating a given solution [2].

The overall process of crystallization from a supersaturated solution is considered to consist of the basic steps of nucleus formation or nucleation and of crystal growth. If the solution is free of all solid particles, foreign whether or of the crystallization substance, then nucleus formation must first occur before crystal growth starts. New nuclei may continue to form while the nuclei present are growing. The driving force for the nucleation step as well as the growth step is supersaturation [1].

2.4.1 Nucleation

The condition of supersaturation or supercooling alone is not sufficient cause for a system to begin to crystallize. Before crystals can develop there must exist in the solution a number of minute solid bodies, embryos, nuclei or seeds that act as centres of crystallization [2]. Nucleation may occur spontaneously or it may be induced artificially. However, it is not always possible to decide whether a system has nucleated of its own accord or whether it has done so under influence of some external stimulus.

2.4.1.1 Solubility and crystal size.

In a solution at a given temperature, the thermodynamic different between small and large particles or crystals is that the small particle has a significant amount of surface energy per unit mass, whereas the larger particle does not. As a result, the solubility of a small crystal, of less than micrometer size, is greater than that of a larger-size crystal [1].

2.4.1.2 Homogeneous nucleation

As a result of rapid random fluctuations of molecules in a homogeneous solution, the molecules may come together and associate into a cluster. This loose aggregate may quickly disappear. However, if the supersaturation is large enough, then enough particles may associate to form a nucleus which can grow and become oriented into a fixed lattice to form a crystal. The number of particles of particles needed to form a stable nucleus ranges up to a few hundred. In solutions with high supersaturation and no agitation, homogeneous nucleation may be important [1].

2.4.1.3 Contact nucleation.

This is due to two types of contact nucleation. In the first type, the formation of new nuclei by contact nucleation is due to interference of the contacting agent (walls of a container or agitator blades) with clusters of solute molecules becoming organized into the existing crystals and by actual breakage of microscopic growths on the surface of the growing crystals. In the second type, the formation of nuclei occurs in collisions between crystals. The intensity of agitation is an important factor in contact nucleation [1].

2.4.1.4 Nucleation in commercial crystallizers

In commercial crystallizer, supersaturation is low and agitation is used to keep the crystals suspended. At low supersaturation the crystal growth rate is at the optimum for more-uniform crystals. The predominant mechanism is contact nucleation. Homogeneous nucleation is largely absent because of the agitation and low supersaturation [1].

2.4.2 Crystal growth theories

If the solubility data for a substance in a particular solvent are known, it is a simple matter to calculate the maximum yield of pure crystals that could be obtained by cooling or evaporating a given solution. The calculated yield will be a maximum, because the assumption has to be made that the final mother liquor in contact with the deposited crystals will be just saturated. The yield will refer only to the quantity of pure crystals deposited from the solution, but the actual yield of solid material may be slightly higher than that calculated, because crystal masses invariably retain some mother liquor even after filtration [2].

The overall process of crystallization from a supersaturated solution is considered to consist of the basic steps of nucleus formation or nucleation and of crystal growth. If the solution is free of all solid particles, foreign whether or of the crystallization substance, then nucleus formation must first occur before crystal growth starts. New nuclei may continue to form while the nuclei present are growing. The driving force for the nucleation step as well as the growth step is supersaturation [1].

As soon as stable nuclei have been formed in a supersaturated or supercooled system, they begin to grow into crystals of visible size. The surface energy theories are based on the postulation that the shape a growing crystal assumes is that which has a minimum surface energy. The mathematical analysis of the operation is similar to that used for other diffusional and mass transfer processes. The suggestion by Volmer (1939)

that crystal growth was a discontinuation process, taking place by adsorption, layer by layer, on the crystal surface led to the adsorption-layer theories, several notable modifications of which have been proposed in recent year [2].

2.5 Scanning Electron Microscope

Electron Microscopes were developed due to the limitations of Light Microscopes which are limited by the physics of light to 500x or 1000x magnification and a resolution of 0.2 micrometers. In the early 1930's this theoretical limit had been reached and there was a scientific desire to see the fine details of the interior structures of organic cells (nucleus, mitochondria...etc.). This required 10,000x plus magnification which was just not possible using Light Microscopes [12]. The first Scanning Electron Microscope (SEM) debuted in 1942 with the first commercial instruments around 1965.

Scanning electron microscope (SEM) is a type of electron microscope capable of producing high resolution images of a sample surface. Due to the manner in which the image is created, SEM images have a characteristic three-dimensional appearance and are useful for judging the surface structure of the sample.

2.5.1 Scanning process

In a typical SEM electrons are thermionically emitted from a tungsten or lanthanum hexaboride (LaB6) cathode and are accelerated towards an anode; alternatively electrons can be emitted via field emission (FE). Tungsten is used because it has the highest melting point and lowest vapour pressure of all metals, thereby allowing it to be heated for electron emission. The electron beam, which typically has an energy ranging from a few hundred eV to 50 keV, is focused by one or two condenser lenses into a beam with a very fine focal spot sized 1 nm to 5 nm. The beam passes through pairs of